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乙醛酸化学镀铜的工艺与机理研究

Technical and Mechanistic Investigation for Electroless Copper Plating Using Glyoxylic Acid as Reducing Agent

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Technical and Mechanistic Investigation for Electroless Copper Plating Using Glyoxylic Acid as Reducing Agent

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摘要

化学镀铜技术已获得广泛的应用。迄今为止，化学镀铜过程大多采用甲醛作为还原剂，而甲醛是对人体和环境有害的物质，必须被其他还原剂所取代。况且，甲醛化学镀铜技术仍存在某些问题，如铜沉积速率较低，难以满足镀厚铜的需要；镀液稳定性不够；镀层因夹杂着Cu_2O等杂质而使其物理性质变差。本文以乙醛酸取代甲醛作为化学镀铜的还原剂，进行以下几方面的研究：

（1） 工艺参数对乙醛酸化学镀铜的沉积速率以及对镀层结构性能的影响。着重研究溶液 pH 值和反应温度对铜沉积速率、镀液稳定性和镀层形貌与结构的影响，以及添加剂 2,2 ´ –联吡啶和亚铁氰化钾的作用。同时测定了不同沉积条件下得到的铜镀层的电阻率，探讨影响电阻率的因素。

（2） 乙醛酸化学镀铜过程的电化学研究。着重研究乙醛酸氧化和铜络合离子还原的电化学过程，以及添加剂对电化学氧化和还原过程的影响，有关实验结果对解释乙醛酸化学镀铜机理有一定帮助。

本研究中用的化学镀溶液的基本组成为：$CuSO_4 \cdot 5H_2O$ 28g/L (0.112mol/L)，络合剂Na_2EDTA 44g/L (0.118 mol/L)，乙醛酸 9.2g/L (0.1mol/L)，2,2 ´ - 联吡啶 10mg/L，亚铁氰化钾 10mg/L。化学镀过程的动力学研究采用传统的工艺实验方法和电化学方法、在不同条件下得到的沉积层的结构、组成与形貌分别用X射线衍射、XPS和SEM观测。得到主要的结果如下：

（1）以乙醛酸化学镀铜溶液的组成和pH值对铜沉积速率有明显的影响，只有当pH值在 11~13 范围内才可获得较好的铜镀层，随着pH的提高镀液的稳定性降低。Cu^{2+}浓度在 0.03～0.2 mol/L 范围内，其反应级数约为 0.63。过量的乙醛酸将导致反应速率的下降，其浓度大于 0.1mol/L时，反应级数为－0.07。络合剂明显过量也将降低铜的沉积速率，当Na_2EDTA浓度大于 0.118mol/L时，其反应级数为－0.1。铜的沉积速率随温度升高而增大，表观活化能为 37kJ/mol。添加剂的用量很小，但能产生明显的动力学效应和形态学效应，适量的添加剂可以显著增大乙醛酸化学镀铜的速率，并提高镀液的稳定性。

（2）在本论文确定的实验条件下，铜镀层呈面心立方多晶结构，没有发现

镀层中含有 1 价铜和 2 价铜。所得镀层电阻率在 2.4μΩ·cm^{-1}左右。镀层电阻率受镀铜溶液的组成、pH值和温度的影响。

（3）电化学实验发现，乙醛酸在铜电极上的阳极氧化大约在－0.8～－0.4V的电位区发生，但受溶液 pH 值的影响。当 E ＞ －0.55V，氧化过程受溶液中扩散控制，电极电位更正时，阳极上同时出现其他过程。当 E ＜ －0.8V 时乙醛酸在铜电极上还原。络合剂 EDTA 的存在对乙醛酸的阳极氧化有抑制作用，可能是由于 EDTA 与乙醛酸在铜电极上竞争吸附所致。提高温度能促进乙醛酸的氧化，由氧化电流与温度的关系得到乙醛酸电化学氧化的表观活化热约为 25 kJ / mol。

（4）在Cu^{2+}和$EDTA^{2-}$共存的体系中，当电极电位E＞－1.0V，还原电流是由游离Cu^{2+}的还原引起的，而E＜－1.0V的还原电流则是络离子的还原引起的。络合剂的存在使得Cu^{2+}离子不会从碱性介质中沉淀出来，但过量的络合剂会降低铜的沉积速率。提高温度能促进铜离子的还原，铜离子还原的表观活化热约为 17 kJ/mol。

（5）添加剂 2，2´-联吡啶和亚铁氰化钾单独存在时，对乙醛酸的阳极氧化都有抑制作用, 而对铜离子的阴极还原的影响却不大。这两种添加剂联合使用，会增强对乙醛酸氧化的抑制效果, 有利于提高化学镀铜溶液的稳定性; 与此同时，促进了铜离子的阴极还原。两种添加剂共存时的协同作用机理值得进一步研究。

关键词：化学镀铜；乙醛酸；沉积速率；镀层电阻率；电化学机理

Abstract

Electroless copper plating have been extensively applied in various fields. Until now, formaldehyde has almost always been the reducing agent in electroless copper plating, which is harm to environment and human body so that it is essential to find a substitute for formaldehyde. Moreover, the development of electroless copper deposition remains to face many challenges such as lower deposition rate, less stable solution, higher resistance of the copper deposits due to mixing the impurities of Cu_2O and others. In this work the technical and mechanistic investigation was carried out for electroless copper plating using glyoxic acid as reducing agent, the focus was put on the following:

(1) The effects of technical parameters on the deposition rate and the structure of the deposites, especially the influences of pH value and temperature of bath on the deposition rate and solution stability, morphology and structure of the deposites, as well as the influnces of using 2,2´-dipyridine and $K_4Fe(CN)_6$ as additives. The electrical resistivity of the deposites was measured so as to study its affecting factors .

(2) Electrochemical studies of electroless copper plating. The electrochemical processes of CHOCOOH oxidation and Cu^{2+} reduction, as well as the functions of additives on the electrochemical oxidation and reduction were studied. The results will be helpful to explore the mechanism of electroless copper plating.

The composition of the bath used is as follows: $CuSO_4 \cdot 5H_2O$ 28g/L (0.112mol/L)，complexing agent Na_2EDTA 44g/L (0.118 mol/L)，glyoxic acid 9.2g/L (0.1mol/L)，2,2´-dipyridine 10mg/L and $K_4Fe(CN)_6$ 10mg/L。The kinetics of the deposition processes was determined by traditional technical methods and electrochemical methods, the structures , components and morphologies of the deposits obtained in different conditions were examined by X-ray diffraction, XPS and SEM，respectively. The main results are outlined as follows:

(1) In electroless copper plating using glyoxic acid as reducing agent, the components and pH value of the bath have a remarkable effect on the deposition rate.

The better copper deposits can be got. only when the pH value is controlled at 11~13 , increasing pH value will make the solution unstable. The reaction orders of [Cu^{2+}] was estimated about 0.63 when the [Cu^{2+}] was varied from 0.03～0.2 mol/L. Excess of glyoxic acid leads to decreasing deposition rate, its reaction orders was estimated about –0.07 when its concentration was higher than 0.1 mol/L. In the solution containing excessive EDTA, the deposition rates decrease with rising EDTA concentration, and .its reaction orders was estimated about –0.1 if EDTA concentration was higher than 0.118 mol/L.

Increasing the temperature of the bath will enhance the deposition rate, the apparent heat of activation of deposition reaction was estimated as 37kJ/mol.

Although a little amount of 2,2 ´ -dipyridine 10mg/L and $K_4Fe(CN)_6$ were used as additives, both their kinetic and morphological effects are evident. Appropriate amount of 2,2 ´ -dipyridine 10mg/L and $K_4Fe(CN)_6$ will not only increase the deposition rate, but also enhance the stability of the bath.

(2) the deposits obtained in this work was found to be polycrystalline *f.c.c* copper , in which no Cu_2O or CuO was detected. Its electrical resistivity is about 2.4μ Ω • cm^{-1}, depending on the deposition conditions used.

(3) from the electrochemical experiments it was found that the oxidation of CHOCOOH on copper electrode occurred in the potential range of －0.8～－0.4V, the voltammetric curves of the oxidation were affected with the changes in pH values of the solution. The oxidation of CHOCOOH was controlled by diffusion. when $E >$ －0.55V, and other reaction appeared simultanously when the potentials shifted toward more positive. The reduction of CHOCOOH on the copper electrode takes place if $E <$ －0.8V. The presence of $EDTA^{2-}$ in the solution inhabits the oxidation of CHOCOOH on copper electrode, attributed to the co-adsorption of the complexing agent with CHOCOOH .Increasing the bath tempreture promotes the oxidation of CHOCOOH, and from the relationship of the oxidation current and temperature, the apparent heat of activation for the oxidation of CHOCOOH was estimated as 25kJ/mol

(4) In a system containing Cu^{2+} and $EDTA^{2-}$, the reduction current is caused by

free Cu^{2+} ions when $E > -1.0V$, while the reduction current is caused by complex ions of Cu^{2+} when $E < -1.0V$. The presence of complexing agent in the bath prevents Cu^{2+} from precipitation in alkaline solution, however, excess of the ligand will decrease the reduction rate released of cupric complex. Increasing the bath temperature will enhance the reduction and from the relationship of the reduction current and temperature, the apparent heat of activation of the reduction was estimated as 17 kJ/mol.

(5) When 2,2 ´ -dipyridine or $K_4Fe(CN)_6$ was added in the solution alone, they would inhabit the oxidation of CHOCOOH, but affect less on the reduction of cupric ions. When these two additives co-exist in the solution, the oxidation of CHOCOOH are more strongly inhabited, thereby the stability of the bath further raised, on the other hand, the reduction of cupric ions was accelerated. The mechanism how the two additives exert the effect in cooperation with each other needs to be further studied.

Key words: Electroless copper plating ,glyoxylic acid, deposition rate, deposit resistivity, electrochemical mechanism

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第一章 绪论

1.1 化学镀铜技术概况

化学镀是通过溶液中适当的还原剂在金属表面自催化作用下使金属离子进行还原的金属沉积过程。化学镀的实质是氧化还原反应，在镀件表面上仍然发生电子转移过程，只不过是无需接上外电源。与电镀相比，化学镀的优点是：(1) 化学镀可实现各种基体上的金属沉积，包括金属、半导体及非金属；(2)化学镀层厚度均匀，无论工件形状如何复杂，只要采取适当的技术措施，就可以在工件上得到均匀的镀层；(3) 化学镀是自催化化学沉积过程，理论上可获得任意厚度的镀层；(4) 化学沉积得到的镀层致密，具有良好的化学和物理性能。化学镀技术最先用于化学镀镍，目前已经发展到化学镀铜、钴、锡、银、金、钯、铂、以及合金镀和复合镀等，已经在电子、计算机、能源、食品、机械、汽车、石油化工、印刷、模具、纺织等各个工业部门获得广泛的应用[1-6]。

1947 年，Narcus首次报道了化学镀铜的工艺原理[7]，20 世纪 50 年代化学镀铜实现工业化。Cahill于 1957 年公开发表化学镀铜溶液的配方，该镀液以甲醛为还原剂，是碱性酒石酸盐镀浴。20 世纪 50 年代末由于成功采用化学镀铜通孔连接工艺代替当时的空心铆钉工艺，从而为化学镀铜技术开辟了广阔的市场。化学镀铜技术在 20 世纪 60 年代获得长足进步，主要成就表现在：(1) 除酒石酸盐外，还采用了EDTA、烷基醇胺等作为络合剂；(2) 发现一系列有效的稳定剂，显著地提高了化学镀铜溶液的稳定性；(3) 成功开发胶体Sn-Pd商品化技术[8]。化学镀铜技术在 20 世纪 70 年代进入成熟阶段，表现在：化学镀铜溶液非常稳定；形成了印刷电路板镀薄铜、图形镀、加法镀厚铜以及塑料镀等的系列化和规模化；出现了镀液分析调整全自动控制的生产线。20 世纪 80 年代高新技术迅速发展，市场提出对印刷电路板的高精度、高层数和高性能的要求，使化学镀铜技术面临新的挑战，其中孔金属化成为制造高层数、高密度印刷电路的中心环节之一。为了保证产品的可靠性，对化学镀形成的铜沉积层的性能，特别是抗张强度、延展性，提出了十分苛刻的指标。虽然这一时期的化学镀铜仍然采用经典的工艺，但工艺材料和控制技术发生了重大的变革。目前，不仅能在宽广的操作条件下保持化学